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NOTE ON THE KELVIN SCALE TEMPERATURE OF FREEZING WATER.

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NOTE ON THE KELVIN SCALE TEMPERATURE OF FREEZING WATER.*

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The values reported for the triple point temperature of water under atmospheric air pressure cover a range from 273.09 to 273.20 on the thermodynamic scale. The importance of the constant, which may be designated T_0, makes it desirable that its value be known to 0.01 degree or about 1 part in 27000; a degree of precision which is at present difficult to realize. To obtain such exactitude the coefficients of expansion of gases, preferably both at constant pressure and at constant volume, must be known to this degree of certainty. A consideration of the available and comparatively large number of coefficients reported for He, H_2, N_2 indicates that on average no single coefficient may be expected to be more exact than 1 part in 10000 corresponding to 0.03° in T_0. The mean deduced value of T_0 may of course be supposed to represent the true value of T_0 within narrower limits. The difficulties involved in measuring the coefficients are numerous but the more important are connected with the reproducibility of the temperature and pressure expansivity of the gas container, the adsorption of the gas on the container walls, the transfusion or solubility of the gas in the container material, besides all the difficulties of reading the pressures or volumes which require a precision of 1 part in 75000 to realize 0.01° in T_0.

The expansion coefficients of a gas may in themselves be sufficient, if measured at different pressures, to determine T_0 assuming, as at present appears legitimate, that as the pressure (p) approaches zero the gases may be assumed to be in a state where the pressure or volume, at constant volume or constant pressure, is proportional to the thermodynamic temperature. The additional assumption is usually involved that the coefficients vary linearly with the pressure: an assumption which evidently need not necessarily be adopted.

Recourse may also be had to the Joule-Thomson effect, or any other measure of the departure of actual gases from the ideal "perfect" state, to convert the actual coefficients into coefficients which the gases would have in the "perfect" state. Of the three measures of "imperfection" in gases the Joule-Thomson effect and the determination of the pressures at various volumes and temperatures are alone of immediate practical importance since the procedure for

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measuring the Joule, or free expansion, effect has not been sufficiently developed[1] to provide reliable values.

The Joule-Thomson effect provides data immediately applicable for converting constant pressure gas thermometer readings to thermodynamic, or Kelvin temperatures. The effect can also be used to convert constant volume gas thermometer readings to Kelvin temperatures, but independent pressure, volume, temperature properties for the thermometric gases are then required, unless the use of certain forms of Equation of State are permissable.

By far the most painstaking and extensive measurements of the Joule-Thomson effect for any substance have been made by J. R. Roebuck for air.[2] The values of the effect $\left(\frac{dT}{dp}\right)_H$, have been tabulated in Roebuck's 1930 paper and values for the free expansion effect $\left(\frac{\partial u}{\partial v}\right)_T = \lambda$, computed. The latter quantity is immediately applicable for reducing constant volume gas thermometer readings to Kelvin temperatures.

On page 316, section 22, of Roebuck's 1930 paper, Chappius' constant volume expansive coefficient is used to obtain T_0 using the λ coefficients obtained from his μ values. The value of T_0 depends upon being able to compute the integral $\int \frac{\lambda}{T^2} dT$ between the limits T_0 and T_{100}. This Roebuck does in a manner which it appears to me may be improved upon. Incidentally attention is called to an error in Roebuck's final computation of T_0.

The expression for the free expansion effect, λ, may be written, where τ designates T^{-1}:

$$\lambda = -\left(\frac{\partial(p\tau)}{\partial\tau}\right)_v \tag{1}$$

Since by definition the thermometric constant-volume coefficient of a gas is $\frac{p_{100} - p_0}{p_0 100} = \alpha_v$ there results:

$$\alpha_v = \frac{1}{T_0} - \frac{T_{100}}{100p_0}\int_{T_0}^{T_{100}} \lambda d\tau$$

$$T_0 = \frac{1}{\alpha_v + \frac{T_{100}}{100p_0}\int_{T_0}^{T_{100}} \lambda d\tau} \tag{2}$$

On page 588 of Roebuck's 1925 paper use is implicitly made of the assumption that air may be represented to a close approximation in its pressure, volume, temperature properties by the equation $p(v + B) = RT$ where B is given by $\frac{A}{RT} - \beta$. The Joule-Thomson coefficient is given however by the thermodynamic equation:

$$\mu c_p = -\left(\frac{\partial(v\tau)}{\partial\tau}\right)_p \tag{3}$$

where c_p is the constant pressure specific heat. From the equation of state above there results accordingly:

$$\mu c_p = B + \tau\frac{\partial B}{\partial\tau} = \frac{2A}{RT} - \beta \tag{4}$$

The Joule-Thomson coefficients at one atmosphere are used by Roebuck to determine $\frac{2A}{R}$ and β, and the value of $\mu\ c_p$ from T_0 to T_{100} is evaluated. The available constant pressure coefficients at various zero degree pressures are then used to deduce values of T_0 which on averaging give $T_0 = 273.153$.

The computation of $-\int \lambda d\tau$ however, is made by selecting values of λ from a table of values at various pressures corresponding to constant volume, the pressure at zero degrees having the value one atmosphere. These λ values are then plotted in a diagram with τ and integrated between 0 and 100° in 25 degree stages assuming a linear relation in the variables. The value so obtained is 2.309×10^{-6} atmospheres per degree with the pressure at zero equal to one atmosphere. Chappius coefficient was obtained at 1.343 atmospheres, and Roebuck obtains for T_0 the number 272.79. The value is too low, however, because the value of $-\int \lambda d\tau$ used to obtain this value of T_0 was taken for 1 atm. instead of for 1.343 atm. corresponding to Chappius coefficient. The correct value of T_0, assuming Roebuck's vaue of $-\int \lambda d\tau$ to be correct at one atmosphere, is obtained by multiplying 2.309×10^{-6} by 1.343 atm. to bring the integral into correspondence with the Chappius coefficient relative to pressure. The value of T_0 then becomes 273.01 instead of 272.79, as stated by Roebuck.

The method of computing $-\int \lambda d\tau$ employed by Roebuck does not however appear to me to be sound. There is no reason, moreover, why the method employed by Roebuck (and others) for obtaining T_0 from the constant pressure coefficients should not be used. From the equation of state used for the μ c_p data at one atm. (Eq. 4) there results for λ:

$$\lambda = + \frac{R}{(V + B)^2} \frac{\partial B}{\partial \tau} = + \frac{A}{(V + B)^2} \tag{5}$$

Since B is small compared to v (1 in 1700 at 0°) λ may be assumed to vary inversely as v^2.

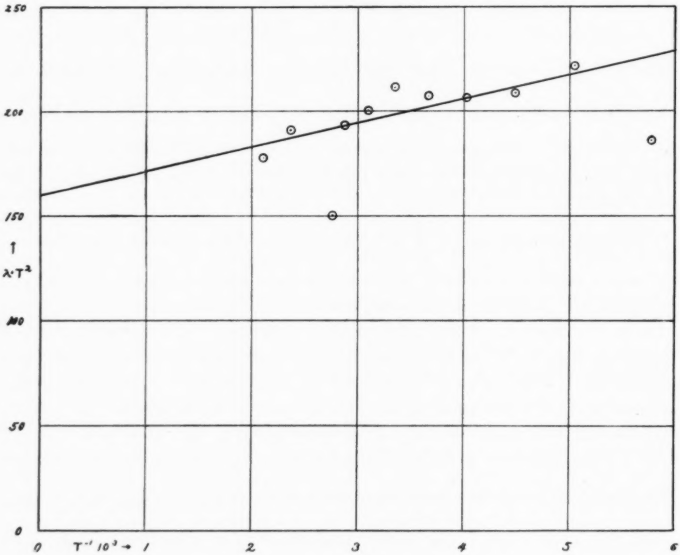

FIG. 1.

Roebuck lists values of λ from $-100°$ to $+200°$ at one atmosphere. To determine A it suffices therefore to assume the gas laws for v and plot the product of λ and T^2 with T^{-1}. A graph of this kind is shown in figure 1. It is to be observed that the data are erratic

but the indication is that λT^2 is linear in T^{-1}. This result is to be expected since the theory of the equation of state for a van der Waals molecular model[3] leads to an expression for B of the form:

$$B = \frac{A}{RT}\left(1 + \frac{a_1}{T} + \frac{a_2}{T^2}\cdots\right) - \beta \tag{6}$$

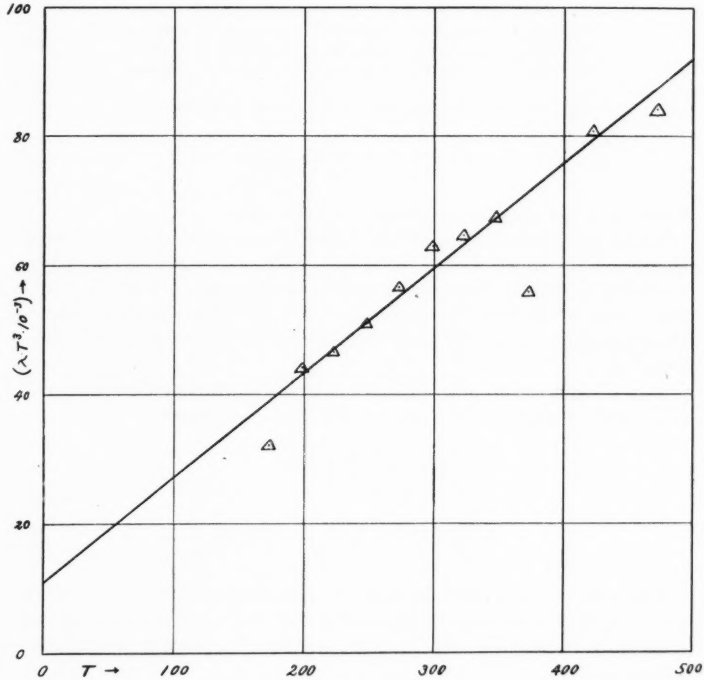

FIG. 2.

From fig. 1 the value of A/R^2 is given by the intercept. In figure 2 λT^3 is plotted with T and here A/R^2 is given by the tangent. The equation finally selected to represent λ for low pressures is:

$$\lambda = \frac{1293}{v^2}\left(1 + \frac{69.8}{T}\right)\frac{\text{atm.}}{\text{cc. per g.}} \tag{7}$$

Table I gives the comparison of the computed values of λ and those given by Roebuck.

TABLE I.

t	−100	−75	−50	−25	0	25
Roebuck	0.006182	0.005681	0.004194	0.003351	0.002779	0.002381
Cal.	0.007536	0.005546	0.004245	0.003350	0.002709	0.002235
Obs.-Cal.	−.001354	+.000135	−.000051	+.000001	+.000070	+.000146

t	50	75	100	150	200
Roebuck	0.001919	0.001597	0.001078	0.001066	0.000795
Cal.	0.001875	0.001595	0.001373	0.001048	0.000825
Obs.-Cal.	+.000044	+.000002	−.000295	+.000018	−.000030

From equation (2) making use of (7) there results:

$$T_0 = \frac{1}{\alpha_v - 9.65 \times 10^{-6} p_0}$$

where p_0 is the pressure of the gas at 0° in atm.

Using the Chappius coefficient 0.00367442 measured at 1.343 atm. there is obtained for T_0 273.116. The mean value of T_0 obtained by Roebuck from the constant pressure coefficients is 273.153. The final mean of T_0 from air is therefore 273.135 which is very close to Buckingham's value (273.13) and mine[4] (273.14) computed some years ago.

It is of interest to note that the μc_p values at one atmosphere are given quite satisfactorily from 0 to 200° by the formula:

$$\mu c_p = \frac{2A}{RT}\left(1 + \frac{3}{2}\frac{a_1}{T}\right) - \beta$$

$$= \frac{912}{T}\left(1 + \frac{76.88}{T}\right) - 1.6105 \frac{\text{atm.}}{\text{cc/g.}} \qquad (8)$$

The value of A is here the same as that obtained from the λ values but a_1 is 51.26 instead of 69.8 showing that the λ and μ values are not quite consistent. The effect of this on the T_0 values is insignificant however.

In concluding this note it is worth emphasizing that the van der Waal's model of a molecule does not lead to an equation of state conforming to the indications of the available pressure, volume, temperature data.[5] Over short temperature ranges (100° to 150°) this molecular model may suffice, as illustrated in the computations above but errors will be introduced if representations of the type of (8) are assumed valid to very low or very high temperatures.

REFERENCES.

[1] Sears and Keyes, Proc. Nat. Acad. Sci., *2*, 38 (1925).

[2] J. R. Roebuck, These Proceedings, *60*, 537 (1925); 64, 287 (1930).

[3] F. G. Keyes, Chem. Review, *6*, 175-(1929). Equation 7.

[4] F. G. Keyes, J. Am. Chem. Soc., *42*, 54 (1920).

[5] F. G. Keyes and R. S. Taylor, J. Am. Chem. Soc., *49*, 896 (1927); also F. G. Keyes, Chem. Review, *6*, 175 (1929).